DENVER FRONT RANGE STUDY
DIOXINS IN SURFACE SOIL

Study 1: Characterization of Dioxins, Furans and PCBs in Soil Samples Collected from the Denver Front Range Area

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LIST OF ACRONYMS AND ABBREVIATIONS

Ah	aryl hydrocarbon
ATSDR	Agency for Toxic Substances and Disease Registry
CAS	Columbia Analytical Services
D/F	dioxin/furan
EMPC	Estimated Maximum Potential Concentration
HRGC/MS	High Resolution Gas Chromatography/Mass Spectrometry
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MQL	Method Quantitation Limit
MRI	Midwest Research Institute
PARCC	Precision, Accuracy, Representativeness, Comparability, and Completeness
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofuran
PE	Performance Evaluation
ppt	parts per trillion (1 microgram per kilogram)
QA/QC	Quality Assurance/Quality Control
QATS	Quality Assurance Technical Support
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
TEF	Toxicity Equivalency Factor
TEQ	*2,3,7,8*-tetrachlorodibenzo-*p*-dioxin equivalents
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF CHEMICAL ABBREVIATIONS

HpCB	heptachlorobiphenyl
HpCDD	heptachlorodibenzodioxin
HpCDF	heptachlorodibenzofuran
HxCB	hexachlorobiphenyl
HxCDD	hexachlorodibenzodioxin
HxCDF	hexachlorodibenzofuran
OCDD	octachlorodibenzodioxin
OCDF	octachlorodibenzofuran
PeCB	pentachlorobiphenyl
PeCDD	pentachlorodibenzodioxin
PeCDF	pentachlorodibenzofuran
TCB	tetrachlorobiphenyl
TCDD	*2,3,7,8*-tetrachlorodibenzo-*p*-dioxin
TCDF	*2,3,7,8*-tetrachlorodibenzofuran

1.0 INTRODUCTION

Overview of the Issue

Dioxins are a class of compounds that are of potential human health concern because they may pose an increased risk of cancer and other non-cancer adverse health effects at extremely low levels of exposure. As a consequence, regulatory agencies often need to evaluate potential risks from dioxins at sites of regulatory concern, especially sites involved in the manufacture of certain chlorinated pesticides and other chemicals.

However, the occurrence of dioxins in site soils is not always evidence of a site-specific release, because dioxins can be formed and released to the environment from multiple sources. Historically, the largest source has been atmospheric deposition resulting from incineration of medical and municipal organic wastes which have high contents of chlorine (USEPA 1994). In addition, dioxins can be formed from the combustion of many other types of organic precursors such as coal and wood, so dioxins can also be released from power plants, wood burning furnaces, forest fires, etc. (USEPA 1998b).

Because of these multiple potential sources of dioxin release to the environment, it is often difficult to know whether dioxin levels observed in soil at a particular location are attributable to some specific local "point" source (e.g., chemical manufacturing, releases from an on-site incinerator, etc.), or whether the levels represent typical "ambient" or ubiquitous concentrations due to other area or non-point sources. Therefore, information on typical ranges of dioxin levels in ambient soils is needed to scientifically evaluate whether particular sites of regulatory concern are contaminated with dioxins attributable to some site-specific source and release pathway.

As discussed in greater detail below, some studies have measured typical ambient levels of dioxins in soil, but the data from these studies are limited and are of uncertain quality and relevance. Consequently, the current study was planned and performed in order to obtain data that are suitable for supporting comparisons of dioxin levels at a site of concern with levels observed in the general environment.

Definition of Dioxins

"Dioxin" is usually used as a synonym for *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin (TCDD). The toxicity of TCDD is believed to be initiated by binding of the TCDD molecule to a cellular protein referred to as the aryl hydrocarbon (Ah) receptor. However, there are many different chemicals besides TCDD that can bind to this receptor and trigger some or all of the toxic responses that are associated with TCDD exposure. This includes some other members (congeners) of the polychlorinated dibenzodioxin (PCDD) class, as well as some polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), other types of halogenated (e.g., brominated) dioxins and furans, as well as various other chlorinated hydrocarbons (e.g., some chlorinated naphthalenes). For the purposes of this report, the term “dioxins” is meant to refer to the set of 29 congeners in the polychlorinated dioxin/furan/biphenyl group that bind to the aryl hydrocarbon (Ah) receptor and possess toxic characteristics similar to those of *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin (TCDD). These 29 congeners are listed in Table 1.

Not all of these 29 dioxin-like congeners are equally toxic. The relative toxicity of a congener, compared to that of TCDD, is expressed in terms of the Toxicity Equivalency Factor (TEF). Table 1 lists consensus TEF values for mammals (including humans), birds, and fish. These TEF values were developed by a panel of experts assembled by the World Health Organization (Van den Berg et al. 1998). Note that TEFs are often based on limited data, and so they are only approximations of the relative toxicity of each congener, rounded to the nearest half order of magnitude.

In this study and report, greatest emphasis is placed on the 17 PCDD and PCDF congeners with TCDD-like activity. This is because the current USEPA soil screening levels for dioxins (USEPA 1998a) are based only upon these congeners. However, the 12 PCB congeners with TCDD-like activity were included in the study and analyses for reasons of completeness for background characterization, and for comparison to other studies that do include data on PCBs.

Calculation of TCDD-Equivalents in Soil

The aggregate toxicity of a mixture of different dioxins in an exposure medium such as soil is a complex function of the following variables:

Table 1. List of Analytes and TEFs

Class	Target Analyte	TEF		
		Mammals	Birds	Fish
Dibenzo-p-dioxins (PCDDs)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	1	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
	1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
	1,2,3,4,6,7,8-HpCDD	0.01	< 0.001	0.001
	OCDD	0.0001	0.0001	<0.0001
Dibenzofurans (PCDFs)	2,3,7,8-TCDF	0.1	1	0.05
	1,2,3,7,8-PeCDF	0.05	0.1	0.05
	2,3,4,7,8-PeCDF	0.5	1	0.5
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	OCDF	0.0001	0.0001	<0.0001
PCBs	3,3',4,4'-TCB (77)	0.0001	0.1	0.0005
	3,4,4',5-TCB (81)	0.0001	0.05	0.0001
	3,3',4,4'-5-PeCB (126)	0.1	0.1	0.005
	3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
	2,3,3',4,4'-PeCB (105)	0.0001	0.0001	< 0.000005
	2,3,4,4',5-PeCB (114)	0.0005	0.0001	< 0.000005
	2,3',4,4',5-PeCB (118)	0.0001	0.00001	< 0.000005
	2',3,4,4',5-PeCB (123)	0.0001	0.00001	< 0.000005
	2,3,3',4,4',5-HxCB (156)	0.0005	0.0001	< 0.000005
	2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	< 0.000005
	2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	< 0.000005
	2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	< 0.000005

TEF = Toxicity Equivalency Factor

TEF values are consensus estimates recommended by WHO (Van den Berg et al. 1998)

a) the concentration of each congener in the medium
b) the chronic average daily intake of the medium
c) the absorption of each congener from that medium
d) the toxicokinetics (distribution, metabolism, and elimination) of the congeners
e) the relative biological potency of the congeners

Thus, calculation of health risk from exposure to soil that contains a mixture of congeners must take all of these variables into account. However, for purposes of screening-level evaluations of dioxin concentrations in soil samples, it is usually most convenient to calculate the concentration of TCDD-Equivalents (TEQ) present in the soil as the TEF-weighted sum of each of the 29 dioxin-like congeners (17 dioxins and furans, plus 12 PCBs), as follows:

$$\text{TEQ (total)} = \sum_{i=1}^{29} (C_i \cdot TEF_i)$$

In cases where interest is focused on the contribution of PCDDs and PCDFs only (i.e., PCBs not included), the value is calculated as:

$$\text{TEQ (D / F)} = \sum_{i=1}^{17} (C_i \cdot TEF_i)$$

It is important to understand that this application of TEFs to the calculation of soil TEQ values is appropriate only for screening level purposes. This is because TEFs are derived from, and thus should only be applied to, biological endpoints (e.g., embryotoxicity). The soil TEQ approach does not account for the potential influences of differential absorption, metabolism, distribution, and excretion of different congeners from soil, and risk assessors should account for these uncertainties in the interpretation of the soil TEQ values.

Review of Existing Data on Ambient TEQ Levels

Limited data are available in the literature on the concentrations of PCDDs and PCDFs in "background" soil. Data from studies that measured the concentrations of all of the toxicologically relevant *2,3,7,8*-substituted PCDD and PCDF congeners are summarized in Table 2. Results are presented as average parts per trillion (ppt) of TEQ, calculated using the WHO consensus TEF values for mammals (Van den Berg et al. 1998). Non-detects were evaluated by assuming a value of zero, so true values are likely to be somewhat higher. As seen, mean values for rural and urban areas are mainly in the 1-6 ppt range, although some lower and some higher

Table 2. Summary of Background Concentrations of Dioxins and Furans(a)

Category	Reference	Location	Number of samples	Comments	MeanTEQ (b) (ppt)
Rural	BC Environment, 1995	British Columbia	53	background	4
	Kjeller et al., 1991	England	3	agricultural, average of 3 samples taken in 1986, excluded all historic samples	2
	MRI, 1992	Connecticut	34	background	6
	Reed et al., 1990	Minnesota	4	semi-rural, background, but near former site of coal-fired power plant	4
	Rogowski and Yake, 1999	Washington	54	agricultural	<1
	Rogowski et al., 1999	Washington	16	rangeland and forest	2
	Rotard et al., 1994	Germany	41	grassland, plowland forest (hardwood, conifer)	3 42
	Schuhmacher et al., 1997	Catalonia, Spain	30	rural samples near where a hazardous waste incinerator is under construction	1
	Rappe and Kjeller, 1987	Europe	3	rural areas from "various parts of Europe"	2
	Tewhey Associates, 1997	Maine	8	background	3
	USEPA, 1996	Ohio	3	background	1
Urban	NIH, 1995	Maryland	37	urban	2
	USEPA, 1996	Ohio	18	urban	21
	Rogowski et al., 1999	Washington	14	urban	4
	Schuhmacher et al., 1997	Catalonia, Spain	10	urban samples near where a hazardous waste incinerator is under construction	5
Industrial	Rappe and Kjeller, 1987	Europe	2	industrial areas from "various parts of Europe"	166

(a) Adapted from USEPA (2000)

(b) TEQ values calculated using WHO consensus TEF values for mammals (Van den Berg et al. 1998). All values rounded to the nearest ppt to account for uncertainties in the measurements.

values are reported. The range of individual sample values in a study is generally much wider than the range of mean values between studies. For example, the range reported in the BC Environment (1995) study was from less than 1 ppt to 57 ppt (mean = 4 ppt). Likewise, Rotard et al. (1994) reported a range of 1-6 ppt in grassland and plowland, and from 6-150 ppt in forest. Thus, the range of mean values for different studies reported in Table 2 should not be interpreted as defining the range of concentrations that occur in individual grab samples.

In considering these data, it is important to recognize that a number of factors may limit the accuracy and relevance of the data, including the following:

1. Some data are from older studies performed 5 to 10 years ago. Because dioxin emission rates have been tending to decrease over time, older data are inherently less relevant and less applicable than current data.
2. In the past (and even in some current studies), Method Quantitation Limits (MQLs) were often higher than background levels in soil, which prevents reliable quantitation of true background levels. In some cases, MQLs were not even reported or defined.
3. In some studies, only partial sets of the 17 dioxin/furan Ah-agonist congeners were measured. In these cases, the true TEQ (the sum of the 29 Ah-agonists listed in Table 1) is likely to be underestimated.
4. Many studies stratified values according to only two land-use categories: rural and urban. Thus, if there are significant differences in background levels as a function of land-use, application of a two category system may obscure important differences.
5. Variations occurred in the depth of soil samples collected. Because dioxin levels resulting from atmospheric deposition and /or application of herbicides are likely to be higher in surface soil than subsurface soil, studies conducted using different soil depths are difficult to accurately compare.
6. Most soil collections were apparently measured in "bulk" (non-sieved, larger particulate) soil samples. However, both humans and animals are believed to be exposed mainly to the fine fraction (less than 250 micrometers maximum diameter) of soil particles. If dioxin levels are higher in the fine fraction, older "bulk" data may underestimate actual exposure levels.
7. Quality control data were not reported in all studies, making it difficult to judge the accuracy and precision of the data.

Purpose of This Study

Because of the multiple potential sources of dioxin release to the environment, and because of the limitations in the existing database on dioxin levels in ambient soils, this project was planned and performed to characterize existing dioxin concentrations in surface soils from multiple locations and multiple land use categories in the Denver Front Range area. It is expected that the data collected during this study will be used by USEPA risk assessors and risk managers to help determine whether the concentration of dioxins in surface soils at CERCLA sites, RCRA sites, and other sites of potential regulatory concern, are higher than those which occur in similar lands that are not known to be impacted by any specific point sources of dioxin releases.

2.0 METHODS

A detailed description of the rationale, methods, and Standard Operating Procedures (SOPs) used in this study is provided in the Project Plan for the study (USEPA 1999). A summary of key elements of the study design and of the methods employed is presented below.

2.1 Soil Sampling

Study Area

The area selected for investigation in this project encompasses the Denver Front Range area, as defined by a square that is approximately 30 miles on a side, centered approximately on Denver, Colorado. This area encompasses approximately 1,000 square miles, and includes a wide variety of different land uses.

Property Ownership

All soil sampling locations in this study were on governmental (public) lands, including properties controlled by Federal, State, County, or other regional agencies.

Spatial and Land-Use Representativeness

In order to be generally useful, the data set of ambient soil concentration values in Denver area soils must be representative of the range of conditions which exist within the study area. That is, samples from only one area might not be representative either of the typical level or of the range of variability observed over the full study area. To this end, the study area was divided into four quadrants, and efforts were made to distribute sampling locations evenly between the quadrants. Likewise, samples collected from only one type of land use might not be representative, since some land uses might tend to have higher or lower levels of dioxins than others. For the purpose of this study, five different types of land use categories were considered, as defined below:

> Residential - Land that is within 200 feet and adjacent to residential development, but which is not within private yards. This may include public parks, neighborhood greenbelts and trails, and street medians. Schools and playgrounds are not included in this category.
>
> Agricultural - Land that is now, or has been within the past 40-50 years, tilled and used for crop production.
>
> Open space - Land that is greater than 20 acres in area that has not been developed or improved and that is essentially in its natural state with the exception of minor changes, such as hiking trails or dirt access roads; this category may include some lands used for grazing of livestock.
>
> Commercial - Land that is developed and used for commercial purposes, such as shopping centers, restaurants, office buildings, post offices, etc.
>
> Industrial - Land that is used for manufacturing, refining, warehousing, or transportation purposes (e.g., garages, railroads, etc.).

As discussed in the Project Plan (USEPA 1999), the goal was to collect approximately 30 samples from each of these five different land uses, for a total of 150 samples. The actual number of samples collected was as follows:

Table 3. Sample Stratification by Land Use

Land Use	**Target**	**Actual**
Agricultural	30	27
Commercial	30	31
Industrial	30	30
Open Space	30	38
Residential	30	39
Total	150	165

Figure 1 is a map which shows the sampling locations and the land use at each location. As seen, the samples are well-distributed across the study area, helping to ensure that the data are fully representative. More detailed maps of the sampling locations, stratified by quadrant, are presented in Appendix C, along with sample coordinates.

Sampling Depth

Because dioxins nearly always bind tightly to soil, it is expected that any dioxin contamination in soil that has occurred chiefly as result of atmospheric deposition and/or application of herbicides will be restricted to the surface. Thus, surface soil is the exposure medium of chief concern for both human and ecological receptors. Therefore, all soil samples collected for this study were grab samples collected at 0-2 inches in depth.

Soil Types

Soil samples were collected at each designated sampling station without regard to the soil type at that station. However, because dioxin levels could tend to vary as a function of soil type, field observations on the nature of the sample (color, texture, etc.) were recorded, and the total organic carbon level of the sample was measured.

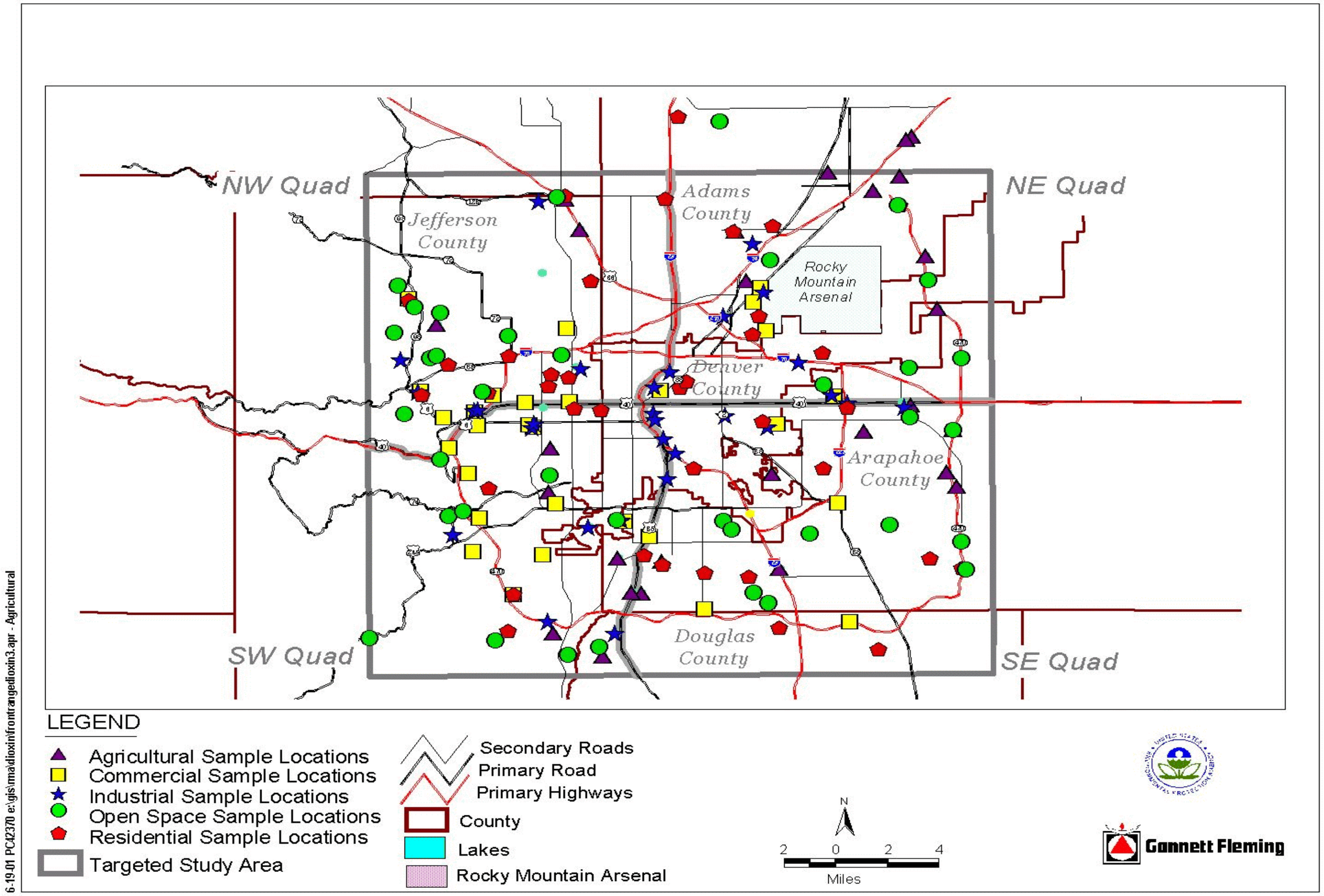
Temporal Bounds

Soil samples were not collected from locations that were known to have been covered with fill or used for borrow material within the last 10 years, since the dioxin content of such recently disturbed areas might not be representative of surrounding undisturbed background areas.

Sample Collection

Samples were collected using clean techniques that included use of disposable stainless steel trowels (one per sampling location) and plastic gloves. A ruler was used to ensure that the actual depth to which soil was collected was within ½ inch of the target (i.e., a bottom depth of no less than 1.5 inches and no greater than 2.5 inches). Loose debris and most gravel or pebbles were removed from the soil sampling site. The surface soil was placed directly into a clean 16-ounce amber glass jar, filled to capacity (about 500 grams of soil), sealed with a teflon-lined lid, and stored in these bottles at room temperature in the dark until shipped in sealed plastic coolers with frozen ice-packs and water temperature tubes that helped ensure no excess heating occurred during transportation to the processing laboratory.

Figure 1. Sampling Locations for Denver Front Range Soil Samples



2.2 Sample Preparation

All soil samples collected in the field were submitted under chain-of-custody to Columbia Analytical Services (CAS) for sample preparation. Each sample was air-dried and weighed, followed by coarse-sieving through a #10 (2 millimeter) stainless steel screen. The fraction passing the coarse screen was referred to as the "bulk" fraction. About 26 grams of the bulk sample was placed in a clean amber glass jar and stored for possible future use, and the remainder was further sieved through a 60-mesh (250 micrometer) stainless steel screen in order to isolate soil particles less than 250 micrometers in diameter. This is referred to as the "fine" fraction. The fine-sieved soil samples were thoroughly mixed, and placed into four new amber sample bottles, with each bottle containing about 26 grams of the fine-sieved soil. These four aliquots of fine-sieved soil were intended to be as identical as possible, for use in reanalysis (if needed) and for establishing intra-laboratory and inter-laboratory reproducibility (precision) for quality control purposes. All processed soil samples were sent under chain of custody to the USEPA Regional Laboratory in Golden, CO, for storage and for organization of samples for later shipments to the analytical laboratory in Kansas City, MO.

The "fine" fraction was isolated for chemical analysis because it is believed that fine soil particles can electrostatically adhere to skin and thus are more likely be ingested by hand to mouth contact than coarse particles. Hence, it is concluded that the fine soil fraction is the most relevant media for use in evaluating human health risk. The bulk soil samples were retained for purposes of evaluating the potential enrichment of TEQ concentrations in the fine-sieved fraction due to small soil particles having greater surface to mass ratios than their bulk soil counterparts. It should be noted that most historic soil sampling studies for dioxins have only evaluated bulk soils, and so consideration needs to be given when comparing historic bulk dioxin results and the results for dioxin TEQs in this study's fine soil samples. If enrichment is present, it would cause the fine soil fractions to have greater concentrations of TEQs than their corresponding bulk counterparts, and bulk soil results would tend to underestimate exposure.

2.3 Sample Analysis

Following sample preparation as described above, samples were submitted by USEPA Region 8 under chain of custody to Midwest Research Institute (MRI) for congener-specific analysis of PCDDs, PCDFs, and PCBs. This type of analysis requires sophisticated extraction and clean-up procedures to accurately measure all of the various forms of PCDDs, PCDFs, and PCBs, as detailed in Standard Operating Procedure 11 of the Project Plan (USEPA 1999). In brief, the congeners are determined using an isotope dilution method via high resolution gas chromatography/mass spectrometry (HRGC/HRMS). Samples are fortified with known quantities of ^{13}C-labeled PCDD/PCDF/PCB isomers and extracted with organic solvents, using two columns so that all 12 PCBs can be retained for analysis. Before cleanup of the extracts, the analytes are exchanged into hexane and fortified with ^{37}Cl-labeled *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin. Finally, the extracts are sequentially partitioned against concentrated acid and base solutions.

The Method Detection Limit (MDL) for this study-specific analytical method was defined as an analyte signal that was 2.5 times the average background signal ("noise"). An estimate of the average signal noise is available for each analyte in each sample, so the MDL varies from sample to sample and from analyte to analyte. The MQL is based partly on the lowest calibration standard used, and was defined as a signal that was 10-times the average signal noise. Because the noise level varied from sample to sample and analyte to analyte, MDLs and MQLs also varied from sample to sample and from congener to congener. Most PCDD/PCDF congeners had MQL values between 0.1 and 3 ppt, and most PCB congeners had MQLs between 0.3 and 15 ppt.

2.4 Quality Assurance

A number of steps were taken to obtain data that would allow an assessment of the quality and reliability of the data collected, so that assessments of the usability of the data could be made and defended. The analytical laboratory routinely processed and analyzed “lots” (batches) of 20 samples at a time. Of these 20 samples, two were used for laboratory control samples (LCS) and blanks. Therefore, 18 samples were usually available for USEPA to submit to MRI as a batch. In general, these 18 samples were comprised of 14 field samples plus four Quality Control (QC) samples, as described below.

<u>Performance Evaluation Samples</u>

Performance Evaluation (PE) samples are samples of a medium that contain known quantities of analyte and that are submitted blind to the analytical laboratory. In this study, three different types of soil PE samples were used. These were obtained from USEPA’s Quality Assurance Technical Support (QATS) laboratory. Nominal values (ppt as TEQ in bulk soil, based on the 17 PCDD/PCDF congeners only) are listed below:

Table 4. Nominal TEQ(D/F) Concentrations in PE Samples

PE Sample (Bulk Soil)	Nominal TEQ(D/F) (ppt)
Native western soil (estimated value)	< 2
Low standard (certified value)	35
Medium standard (certified value)	59

One aliquot of each of these three PE samples from QATS was submitted to the laboratory along with each batch of field samples.

Field Splits and Duplicates

A field duplicate is a second sample of soil collected simultaneously with the first sample. In this case, field duplicates were collected by alternating scoops of soil into two bottles with separate and random sample identification numbers. A field split is a sample that is generated by dividing a single field sample into two parts. As described above, in this study every field sample was dried and sieved by CAS, and this fine material was divided into four essentially identical aliquots of 26 grams each. USEPA Region 8 selected random samples to submit as split samples, and a second bottle of these samples was assigned a new random sample identification number and submitted in random order for analysis by MRI. Analysis of these types of samples provided data on the variability within and between related samples. One sample of this type (either field split or field duplicate) was submitted to the laboratory (blind) with each set of 14 field samples.

Laboratory Quality Control Samples

Internal laboratory quality control samples are samples prepared and run by the laboratory in a non-blind fashion to monitor the performance of the analytical method. Laboratory QC samples included Method Blanks (analyte-free soil), Laboratory Control Samples (similar to PE samples, but the identity and true concentration are known to the laboratory), and optionally Method Duplicates (investigative samples that are split prior to sample preparation at the analytical laboratory). As noted above, two samples in each batch were used by the laboratory for laboratory QC samples.

2.5 Data Validation/Verification

Validation of analytical results was conducted according to SOP 803 (revision 1) of the Project Plan (USEPA 1999). This validation method was tailored to match the site-specific method used to analyze the 29 dioxin-like congeners in soils. An independent contract chemist team, with expertise in validation of PCDD, PCDF, and PCB analytical results, conducted the analytical reviews. Full validation was performed for all samples.

Major analytical factors and QA/QC performance were reviewed against defined Precision, Accuracy, Representativeness, Comparability, and Completeness (PARCC) criteria to ensure that results were reliable and usable for the objective identified in the Project Plan. Narratives were produced for each analytical lot to describe the results of the data validation for that lot. Each data value (i.e., each concentration value) was assigned a data usability flag, if needed, using the data quality flag codes presented in Table 5. In accordance with USEPA data usability guidelines (USEPA 1992), these flags were used for producing two alternative data sets:

1) a <u>semi-quantitative</u> set of results in which congeners that yielded signals below the sample-specific detection limit for that congener (signal/noise ratio less than 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit for that congener, and other flagged data were adjusted according to the rules shown in Table 5. This is referred to in this report as the "**Full**" data set.

2) a <u>quantitative</u> set of results based only on those congeners that have no disqualifying flags (D, NJ, R and LT), or have adjusted quantitative values as described in Table 5. This is referred to in this report as the "**Quant**" data set.

These two datasets were prepared to help evaluate the magnitude of effects of estimated values from the Full dataset on TEQs, and to show how the quantitative subset of results can be properly derived to statistically evaluate the profiles of congeners in soils. In general, the Full TEQ(D/F) results are considered to be the most relevant in evaluating potential health risks from dioxins.

Table 5. Definition, Application, and Uses of Data Flags

Validation Flags	**Meaning of Flags** for Dioxin Analyses in Soils and Tissues by the MRI Lab	Data Usability (a)	
		Full data set used (*semi-quantitative*)	**Quantitative** (qualified sub-set used)
E	Estimated Maximum Potential Concentration; the relative ion abundance ratios did not meet the acceptance limits.	use value	use ½ value
D	EMPC is caused by polychlorinated **D**iphenyl ether interference.	use ½ value	don't use
B	Analyte was detected in associated Method **B**lank, sample concentration <5x MB concentration.	use value	use ½ value
C	Concentration is above upper **C**alibration Standard; result is an estimate, flagged C by lab and J added by validator.	use value	use value
I	Recovery of 13C-labeled **I**sotopic analyte outside of criteria	use value	use value
J	Estimated: e.g., isotopic standard is outside CCAL range, native analyte recovery in LCS is outside criteria, etc.	use value	use ½ value
NJ	Presumptive evidence for the presence of an analyte with an estimated value; if used for 2378-TCDF, see "U" below.	use ½ value	don't use
S	Peak is **S**aturated; result, if calculated, is flagged by the validator as an estimate - "J".	use value	use value
U	**U**nconfirmed: column is not specific for 2,3,7,8-TCDF; confirmation not requested. Validator now uses "NJ" flag.	use value	use ½ value
R	**R**ejected: result is invalid and not usable.	use ½ MDL	don't use
***use of MRI Laboratory's reported "LT" (less than) values* <MQL (10 x Signal:Noise)**			
LT *applied **first** to data, then apply flags!*	"LT" is not a true "flag", but if a LT result is a "**detect**" **above the MDL** (2.5 x Signal:Noise = lab EDL), then	use value	use ½ value
	"LT" is not a true "flag", but if a LT result is a "**non-detect**" **below the MDL** (2.5 x Signal:Noise = lab EDL), then	use ½ EDL	don't use

(a) In accord with concepts in the 1992 USEPA Data Usability for Risk Assessment in Superfund guidance (USEPA 1992), data quality flags are used to produce two data-sets: 1) a "**Full**" set of semi-quantitative results with an **actual** or a **proxy** value for each of the measured congeners; and 2) a more "Quantitative" but limited set of results that has more certain identification and more accurate quantities of congeners which have **no disqualifying flags** (D, NJ, R or LT), but can use **limited proxies** (E, B, J or U). This distinction is made to better understand and limit artifactual impacts of the *less certain **estimated** values* on TEQs, analyzing the degree of this sensitivity to trace-level "noise" by comparing TEQs from these two data sets. In addition, congener profile pattern analysis should only use the analytes that are quantifiable (above the MQL).

3.0 RESULTS

Detailed analytical results for each field sample are presented in **Appendix A1**, and detailed results for each QC sample run as part of this study are presented in **Appendix A2**. Graphical representations are presented in **Appendix B**. The results are summarized below.

3.1 Data Validation Results

Full validation of the data collected during this study found the analytical results for all samples to be usable, as qualified with the appropriate data quality flags.

3.2 TEQ Values in Field Samples

Of the 165 field samples collected during this study, sufficient sample mass was available to sieve and analyze the fine fraction for 162 samples. The Full TEQ(D/F) results for these 162 samples are shown in Table 6 (Panel A). The values for the three other samples (bulk analysis only) are shown in the footnote to Panel A. Maps showing the spatial pattern of all 165 results (fine and bulk), stratified by land use, are presented in Appendix D.

As seen in Table 6, there is a fairly wide range of Full TEQ(D/F) values observed in Denver area soils (fine fraction), from a minimum of less than 0.1 ppt TEQ up to a maximum of 155 ppt TEQ. The distributions all tend to be right skewed, and the log-transformed data all pass the Kolmogorov-Smirnov test for normality ($p > 0.05$) except for the residential data set ($p = 0.008$). This indicates that most of the data may be reasonably approximated by lognormal probability density functions.

Visual inspection of the raw data (Appendix A) suggest that two data points (the maximum value for the commercial and the residential data sets) might be outliers. This was evaluated by a simple outlier test (based on the mean plus 2.5 standard deviations of the log-transformed values), which indicated that these two data points were very unlikely to have been drawn from the same distribution as the remainder of the points in each group. The basis for these two apparent outliers is not known, but might be due to the presence of some specific (but unknown) point source at these two sampling locations. Based on the conclusion that these two samples are not representative of their respective land uses, they were excluded from further analysis. Panel B of Table 6 shows the summary statistics after exclusion of these two data points.

Table 6. Summary Statistics for Full TEQ(D/F) Levels in Surface Soil Samples

Panel A: All Data[a]

Land Use	Statistic						
	N	**Mean ppt**	**Stdev ppt**	**GM ppt**	**GSD**	**Min ppt**	**Max ppt**
Agricultural	27	1.6	1.8	1.0	3.0	0.1	7.7
Commercial	31	10.7	26.5	3.4	3.8	0.4	140.2
Industrial	29	9.8	14.3	4.2	4.0	0.2	54.4
Open Space	37	1.6	2.2	0.9	2.9	0.1	9.1
Residential	38	11.0	26.0	3.5	4.0	0.2	154.7
Total	162	7.0	18.5	2.1	4.2	0.1	154.7

[a] Values above are for 162 samples for which there was sufficient mass to prepare and analyze the fine fraction. Results for 3 samples in which only the bulk fraction was analyzed are as follows:

Open space	N = 1	2.5
Industrial	N = 1	3.7
Residential	N = 1	5.6

Panel B: Two Outliers Excluded

Land Use	Statistic						
	N	**Mean ppt**	**Stdev ppt**	**GM ppt**	**GSD**	**Min ppt**	**Max ppt**
Agricultural	27	1.6	1.8	1.0	3.0	0.1	7.7
Commercial [b]	30	6.4	11.2	3.0	3.2	0.4	57.5
Industrial	29	9.8	14.3	4.2	4.0	0.2	54.4
Open Space	37	1.6	2.2	0.9	2.9	0.1	9.1
Residential [b]	37	7.1	10.2	3.2	3.5	0.2	42.9
Total	160	5.3	9.7	2.0	3.9	0.1	57.5

b Statistics exclude one data point from the commercial data set and one data point from the residential data set that are judged to be outliers

All values are expressed in units of ppt of TCDD-Equivalents (TEQ), based on the results for 17 PCDDs and PCDFs (see Table 1). The TEQ was calculated based on the mammalian TEF values shown in Table 1, using ½ the detection limit for samples that were reported to be present below the detection limit.

Figure 2 is a graphical representation of the distributions of Full TEQ(D/F) in fine soils after the two outliers have been excluded. As seen, while all of the values are relatively low, samples collected on lands that were ranked as agricultural or open space tended to have values somewhat lower than those from commercial or industrial areas. The distribution for residential samples is generally similar to that for commercial properties. In interpreting this finding, it is important to remember that none of the "residential" sampling locations are actually on private residential properties, but rather all are on governmental properties located in or near residential neighborhoods. In some cases, the current land use is more similar to light commercial/industrial than residential (e.g., pump stations, park-and-ride stations). In addition, because a full land use history is not available for most of these properties, it is possible that some of these governmental properties may have been used in the past for activities that tended to increase dioxin levels slightly.

3.3 Contribution of PCBs

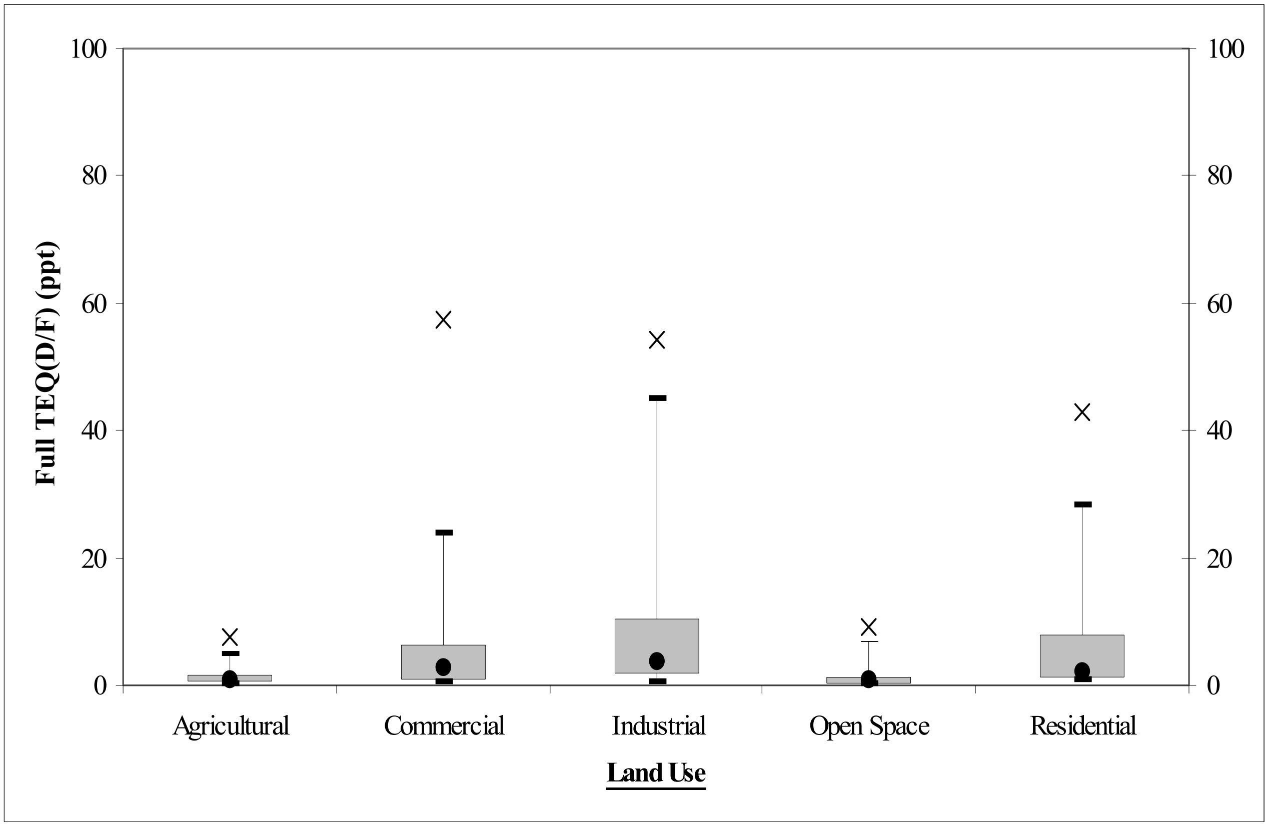
The Full TEQ(D/F) values presented in Table 6 are based on the sum of TEQ values across 17 dioxin/furan congeners. As noted above, some PCBs also posses dioxin-like activity and may contribute to the levels of TEQ in soil. Summary statistics (averaged across samples within a land use category) are presented below:

Table 7. Contribution of PCBs to Total TEQ

Land Use	Full TEQ (ppt)			% PCBs
	D/F	PCB	Total	
Agricultural	1.6	0.3	1.9	18%
Commercial	6.4	2.2	8.5	25%
Industrial	9.8	5.6	15.4	36%
Open Space	1.6	1.2	2.8	43%
Residential	7.1	1.7	8.8	19%
All	5.3	2.1	7.4	29%

As seen, PCBs contribute about 1 ppt or less to the Full TEQ(Total) in agricultural and open space soils, but may contribute about 2-6 ppt in commercial, industrial or residential samples. On average across all samples, PCBs contribute about 29% of the total TEQ (summed across all 29 D/F and PCB congeners).

Figure 2. Range of Full TEQ(D/F) Levels in Denver Front Range Soils



3.4 Contribution of Congeners Below the Quantitation Limit

As noted above, in the calculation of the Full TEQ value for a sample, all congeners that were below the MDL (signal/noise ratio < 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit, and values between the MDL and the MQL were evaluated using the reported value. This is the approach is that is normally used to evaluate chemicals of concern at Superfund sites (USEPA 1989). In order to evaluate the relative contribution of congeners that were either not detected, or else were present at such low concentrations that their true concentration could only be estimated, a second calculation of "Quant" TEQ was performed, which included only those congeners that were detected above the MQL (signal/noise > 10). A comparison of the Full and Quant TEQ values are shown below:

Table 8. Contribution of Congeners Below the MQL

Land Use	Average TEQ(D/F) (ppt)		Average Contribution of Congeners < MQL (ppt)	Average TEQ(Total) (ppt)		Average Contribution of Congeners < MQL (ppt)
	Quant	Full		Quant	Full	
Agricultural	1.0	1.6	0.6 (38%)	1.3	1.9	0.6 (32%)
Commercial	5.3	6.4	1.1 (17%)	7.4	8.5	1.1 (13%)
Industrial	7.9	9.8	1.9 (19%)	11.6	15.4	3.8 (25%)
Open Space	1.3	1.6	0.3 (19%)	2.2	2.8	0.6 (21%)
Residential	5.9	7.1	1.2 (17%)	7.3	8.8	1.5 (17%)
All	4.3	5.3	1.0 (19%)	5.9	7.4	1.5 (20%)

As seen, the average contribution of congeners below the MQL to TEQ is about 1.0 ppt (D/F only) to 1.5 ppt (D/F plus PCBs), which corresponds to an average of about 19% to 20% of the total TEQ. This supports the conclusion that the Full TEQ results are not unduly influenced by congeners below the MQL, even at these relatively low soil levels. At higher soil levels, the relative contribution of congeners below the MQL is expected to decrease.

3.5 Comparison of Bulk to Fine

As noted earlier, all field soil samples were prepared by sieving to isolate the “fine” fraction of particles less than 250 micrometers in diameter, since it is believed that this size fraction is likely to be of greater relevance to human exposure than the bulk fraction. However, since most other studies of dioxin concentrations in soil have used un-sieved soil, a number of samples of bulk soil were also analyzed to allow a comparison of concentration values in the bulk and fine fractions. The results are shown in Figure 3. As seen, there is an enrichment of TEQ in the fine soil compared to the bulk soil for some samples, but on average the data tend to cluster about a line with a slope of 1.0. This indicates that, on average, the TEQ values based on the bulk sample are similar to those based on the fine sieved soil.

3.6 Contribution of Specific Congeners

The congener composition of a soil sample may provide useful information about the source of the dioxin contamination, and helps to reveal which specific congeners are contributing the majority of the risk.

Appendix A shows the relative (percent) contribution of each of the 29 congeners to the total TEQ in each of the samples from the Denver Front Range area. The mean contribution of each congener (percent contribution within a sample averaged across all samples) to TEQ is summarized in Table 9. As seen, most of the Full TEQ(Total) is contributed by PCB-126, *1,2,3,7,8*-PeCDD, and *1,2,3,4,6,7,8*-HpCDD, with additional contributions from *2,3,4,7,8*-PeCDF, *1,2,3,6,7,8*-HxCDD, and *2,3,7,8*-TCDD.

Appendix B1 presents a series of graphs showing the absolute chemical concentrations and TEQ contributions of each of the 29 congeners in each of the field soil samples collected during this study. Appendix B2 shows the aggregate concentrations and TEQ contributions for each of the five homologue classes of the 17 TCDD-like dioxins and furans. Appendix B3 shows the relationships between aggregate concentrations and TEQ contributions of dioxins compared to furans. Appendix B4 presents similar concentration graphs for QA samples. In all cases, greater emphasis is placed on the quantitative concentration data than the full concentration data for evaluation of congener concentration profiles.

Figure 4 summarizes the average quantitative congener concentration pattern in Front Range soils. The upper panel shows congeners in the PCDD/PCDF class, while the lower panel shows congeners in the PCB class. As seen in the upper panel, the primary congener in the dioxin/furan class is usually OCDD, along with lower amounts of OCDF, *1,2,3,4,6,7,*8-HpCDD, and *1,2,3,4,6,7,8*-HpCDF. As seen in the lower panel, several PCBs are usually present, primarily 77, 105, 118, 156, and 167.

A more detailed and quantitative analysis of the congener concentration values in surface soil samples from Front Range soils, as well as other sites in the Denver Front Range area where dioxin soil sampling has been conducted, will be presented in a subsequent report.

Figure 3. Comparison of TEQ Values in Bulk and Fine Soil

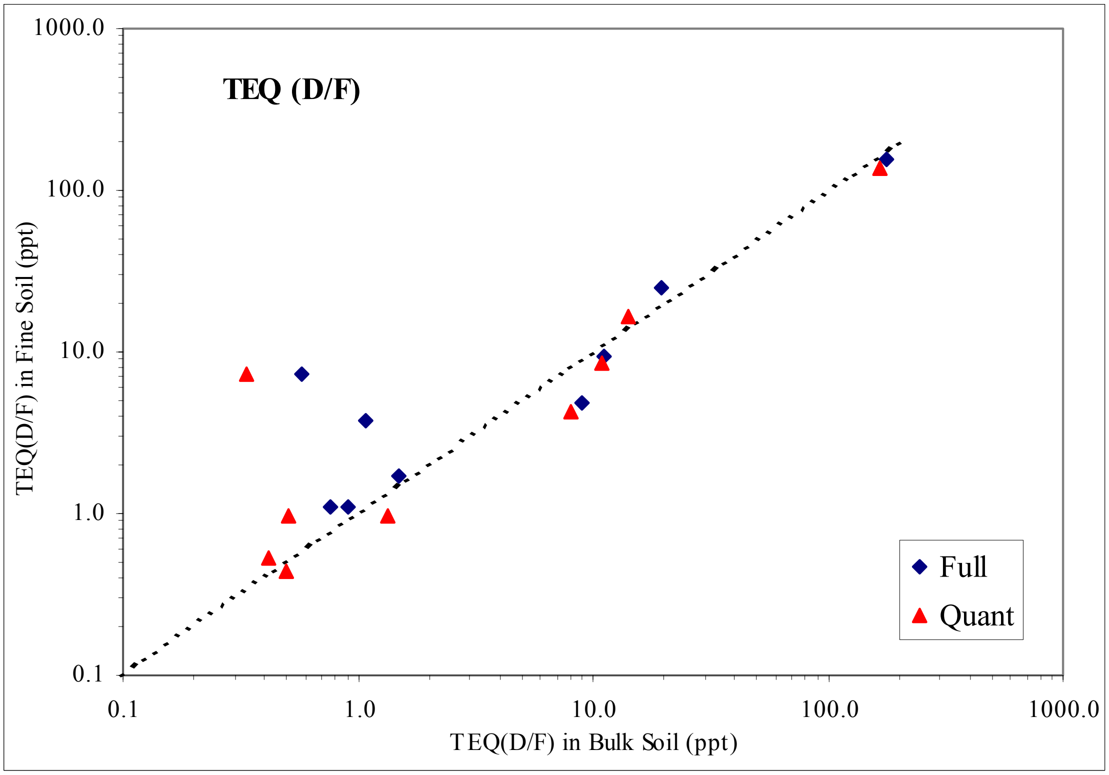
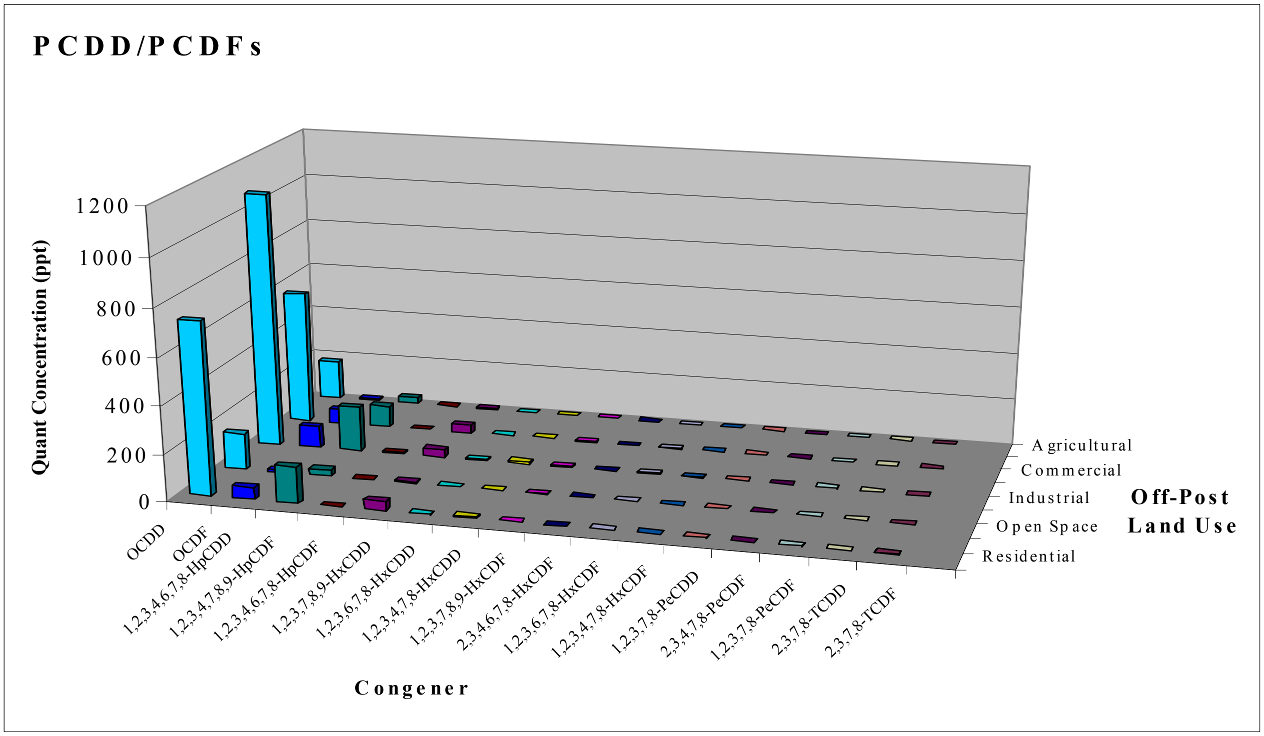


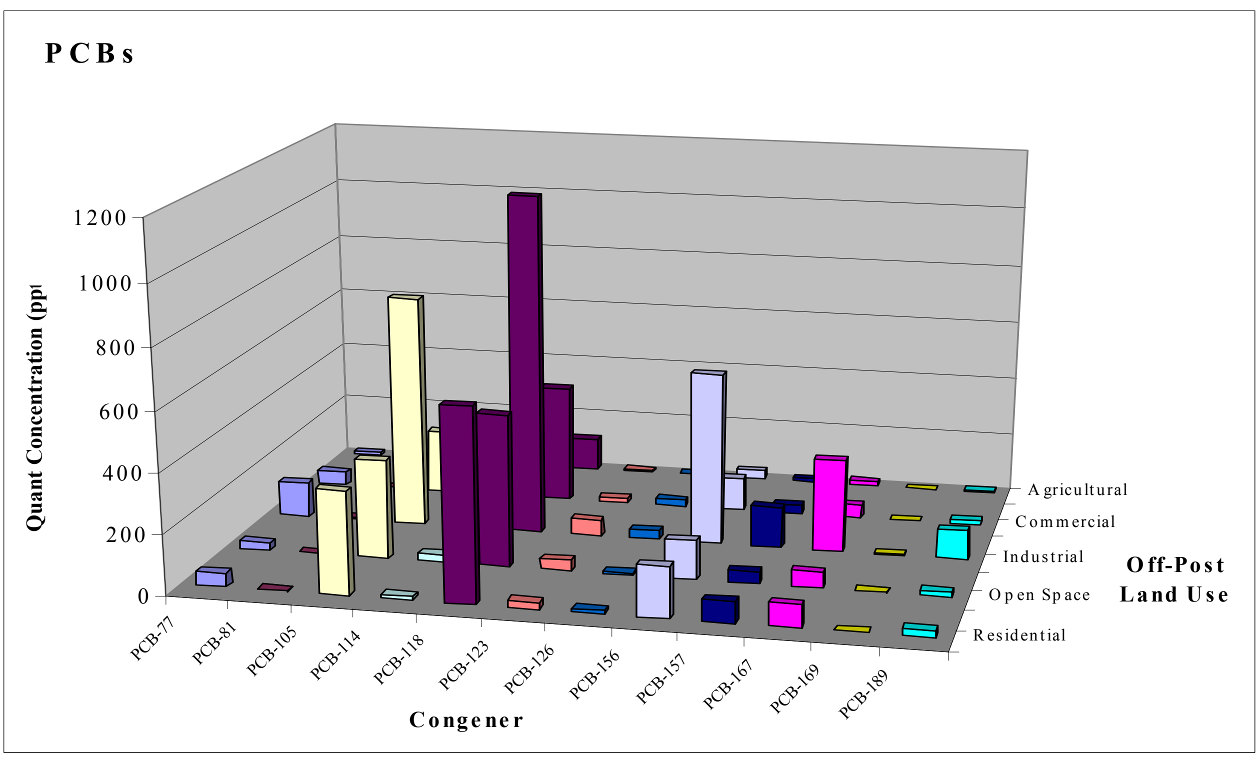
Table 9. Relative Contribution of Congeners to Full TEQ(Total)

Analyte	Mean Contribution to Full TEQ(Total)					
	Agricultural	Commercial	Industrial	Open Space	Residential	All
2,3,7,8-TCDF	0.8%	0.6%	0.4%	0.7%	0.5%	0.6%
2,3,7,8-TCDD	4.3%	9.6%	3.7%	2.7%	7.0%	5.5%
1,2,3,7,8-PeCDF	0.7%	0.6%	0.4%	0.7%	0.5%	0.6%
2,3,4,7,8-PeCDF	12.5%	8.0%	8.9%	9.8%	8.3%	9.4%
1,2,3,7,8-PeCDD	19.6%	20.0%	16.1%	20.4%	18.5%	19.0%
1,2,3,4,7,8-HxCDF	2.7%	2.2%	2.2%	2.2%	2.1%	2.3%
1,2,3,6,7,8-HxCDF	3.1%	2.3%	2.2%	2.9%	1.8%	2.4%
2,3,4,6,7,8-HxCDF	4.0%	3.0%	2.7%	2.9%	2.6%	3.0%
1,2,3,7,8,9-HxCDF	4.7%	2.0%	1.8%	4.7%	2.0%	3.0%
1,2,3,4,7,8-HxCDD	3.2%	2.7%	3.2%	3.4%	2.9%	3.1%
1,2,3,6,7,8-HxCDD	5.1%	5.6%	5.7%	5.1%	6.1%	5.5%
1,2,3,7,8,9-HxCDD	3.7%	3.8%	4.0%	3.7%	3.9%	3.8%
1,2,3,4,6,7,8-HpCDF	2.3%	2.7%	2.7%	1.6%	2.9%	2.4%
1,2,3,4,7,8,9-HpCDF	0.3%	0.6%	0.2%	0.3%	0.3%	0.3%
1,2,3,4,6,7,8-HpCDD	12.1%	14.7%	16.9%	11.9%	16.8%	14.5%
OCDF	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
OCDD	0.9%	1.0%	1.3%	0.9%	1.2%	1.1%
PCB-77	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
PCB-81	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PCB-105	0.5%	0.6%	0.6%	0.7%	0.7%	0.6%
PCB-114	0.1%	0.2%	0.1%	0.2%	0.2%	0.1%
PCB-118	1.0%	1.3%	1.1%	1.3%	1.5%	1.3%
PCB-123	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PCB-126	16.9%	16.6%	23.3%	21.9%	18.2%	19.4%
PCB-156	0.9%	1.2%	1.4%	1.3%	1.3%	1.2%
PCB-157	0.2%	0.3%	0.4%	0.3%	0.4%	0.3%
PCB-167	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
PCB-169	0.3%	0.2%	0.2%	0.4%	0.2%	0.3%
PCB-189	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
Dioxins/Furans	80.0%	79.5%	72.7%	73.8%	77.5%	76.6%
PCBs	20.0%	20.6%	27.3%	26.2%	22.5%	23.5%
All	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

Congeners which contribute 5% or more to the average total TEQ have been shaded

Figure 4. Average Congener Concentration Profile in Front Range Soils





3.7 Quality Control Samples

Quality control samples that were analyzed as part of this study indicate that the data are reliable and accurate, as described below.

Method Blanks

Full TEQ(Total) values for 16 method blanks averaged 0.5 ppt (range = 0.1-1.8 ppt). This indicates that there is no significant source of PCDD, PCDF, or PCB contamination within the analytical laboratory.

Splits and Duplicates

The results for split and duplicate pairs were generally in good agreement, as shown in Figure 5. Summary statistics for Full TEQ(D/F) are presented below, stratified into two bins depending on the TEQ concentration, as described in the Project Plan (USEPA 1999):

Table 10. Evaluation of Precision

	TEQ <= 25 ppt		TEQ > 25 ppt	
Type	**N**	**Average Delta (ppt)**	**N**	**Average RPD (%)**
Duplicates	8	2.3	2	21%
Splits	11	0.3	1	1%

For samples with a TEQ concentration less than 25 ppt, the average absolute difference between samples pairs is about 0.3 to 2.3 ppt TEQ, well within the acceptability criterion of 1 MQL (about 5 ppt TEQ) that was established by the Project Plan (USEPA 1999) for samples with concentration values less than 5-times the MQL. For samples with TEQ values above 25 ppt (5-times the MQL), the Relative Percent Difference (RPD) ranges from 1% to 21%, also well within the acceptance criterion of 30% established by the Project Plan (USEPA 1999).

Performance Evaluation Samples

Analytical results for the soil standards (PE samples) obtained from the USEPA QATS laboratory are summarized in Table 11.

Figure 5. Comparison of Duplicate and Split Results

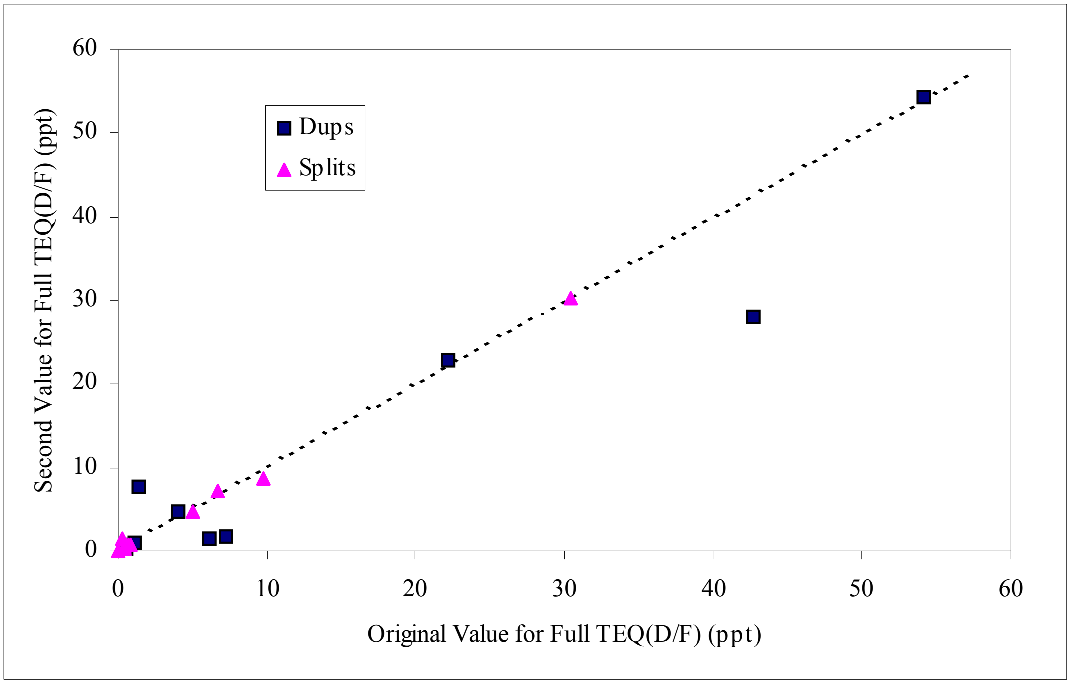


Table 11. Evaluation of Accuracy Using Certified PE Samples

PE Sample	Certified Conc. (ppt)	N	Measured TEQ(D/F) (ppt)	
			Full	Quant
Low Standard (bulk)	35	2	47.5 ± 3.2	47.3 ± 3.1
Medium Standard (bulk)	59	3	74.5 ± 1.4	73.5 ± 0.3

As seen, the measured TEQ values for bulk PE samples are somewhat higher than but are still in reasonable accord with the expected (nominal) values. Precision between multiple analyses of the PE samples was good (typically within a few percent).

Multiple samples (N=22) of the "Clean Soil" PE sample provided by the QATS laboratory were also analyzed on an on-going basis throughout the study. This is the soil used by QATS contractors for spiking with TCDD-like dioxin and furan congeners to produce the PE standard soils. This soil sample was estimated to contain less than 2 ppt TEQ in the bulk fraction, but this was not a certified value. The samples of Clean Soil analyzed in this study were sieved to isolate the fine fraction before analysis, so the expected value in the fine fraction is not known. However, analytical results were low (1.6 ± 0.4 ppt Full TEQ(D/F) and 1.8 ± 0.4 ppt Full TEQ(Total)), consistent with the estimated values in the bulk soil. Because these samples were submitted to CAS in parallel with field samples, these results also establish that there is no significant source of contamination during the sample preparation or the sample analysis steps.

Laboratory Spikes

Sixteen different laboratory spikes were analyzed in association with the field samples from the Front Range study. Spike concentrations were 20 ppt for TCDD and TCDF, 100 ppt for each of the penta-, hexa- and hepta-CDDs and -CDFs, and 200 ppt for OCDD, OCDF, and each of the PCBs. Based on this spiking mixture, the nominal TEQ(D/F) is 250 ppt, and the nominal TEQ(Total) is 272.5 ppt. Recovery of individual PCDD/PCDF congeners averaged across all samples ranged from 75% to 108%, with an average of 93% across all samples and all PCDD/PCDF congeners. Recovery of individual PCBs averaged across all samples ranged from 103% to 120%, with an average of 107% across all samples and all PCB congeners. When expressed as Full TEQ, recovery across different samples ranged from 92% to 103% (mean = 98%) for TEQ(D/F), and from 93% to 104% (mean = 99%) for TEQ(Total). This indicates that matrix interference is not likely to be of concern.

4.0 DISCUSSION

4.1 Dependence of Dioxin Levels on Land Use

As seen in Figure 2 and Table 6, Full TEQ levels for dioxins and furans in area soils are generally low. However, the distributions of TEQ levels tend to be somewhat higher in commercial, industrial, and residential areas than in open space or agricultural areas. The distributions of values in each land category were compared using Kruskal-Wallis one-way analysis of variance (ANOVA) on ranks. The results indicated that differences between land uses were statistically significant ($p < 0.001$). Multiple pair-wise comparisons using the Mann-Whitney Rank Sum Test were performed to isolate the groups which were different from each other. The results were as follows:

Table 12. Statistical Differences Between Land Uses

	Agricultural	Commercial	Industrial	Open Space
Commercial	Yes ($p < 0.01$)			
Industrial	Yes ($p < 0.01$)	No ($p = 0.264$)		
Open Space	No ($p = 0.664$)	Yes ($p <0.01$)	Yes ($p < 0.01$)	
Residential	Yes ($p < 0.01$)	No ($p = 0.772$)	No ($p = 0.258$)	Yes ($p < 0.01$)

As seen, the land use data sets fall into two groups: open space and agricultural lands are not statistically different from each other, but are different from the industrial, commercial and residential data sets. Conversely, the industrial, commercial and residential data sets are not different from each other, but are different from the open space and agricultural data sets. Combining the data into these two groups (Open Space/Agricultural, and Commercial/Industrial/Residential) yields the following summary statistics:

Table 13. Summary Statistics for Full TEQ(D/F) for Combined Land Uses

Statistic	Agricultural and Open Space	Commercial, Industrial and Residential
N	64	96
Mean	1.6	7.7
Stdev	2.0	11.8
5th	0.2	0.6
25th	0.5	1.4
50th	0.9	3.0
75th	1.4	7.6
95th	6.7	30.5

These values are generally similar to the ranges of TEQ values for rural and urban areas reported in other studies (see Table 2).

As noted above, each sampling location was classified into one of five different land use categories based on an inspection of the sampling location. However, in some cases (35 out of 160), the land use assignment was considered to be uncertain, and a secondary land use category was also identified. Figure 6 compares the distribution of Full TEQ(D/F) values based on the original and the alternative land use assignments. As seen, the distributions are generally similar, indicating that uncertainty in the appropriate land use assignment of specific sampling locations is not likely to significantly alter the basic findings.

4.2 Evaluation of Potential Confounders

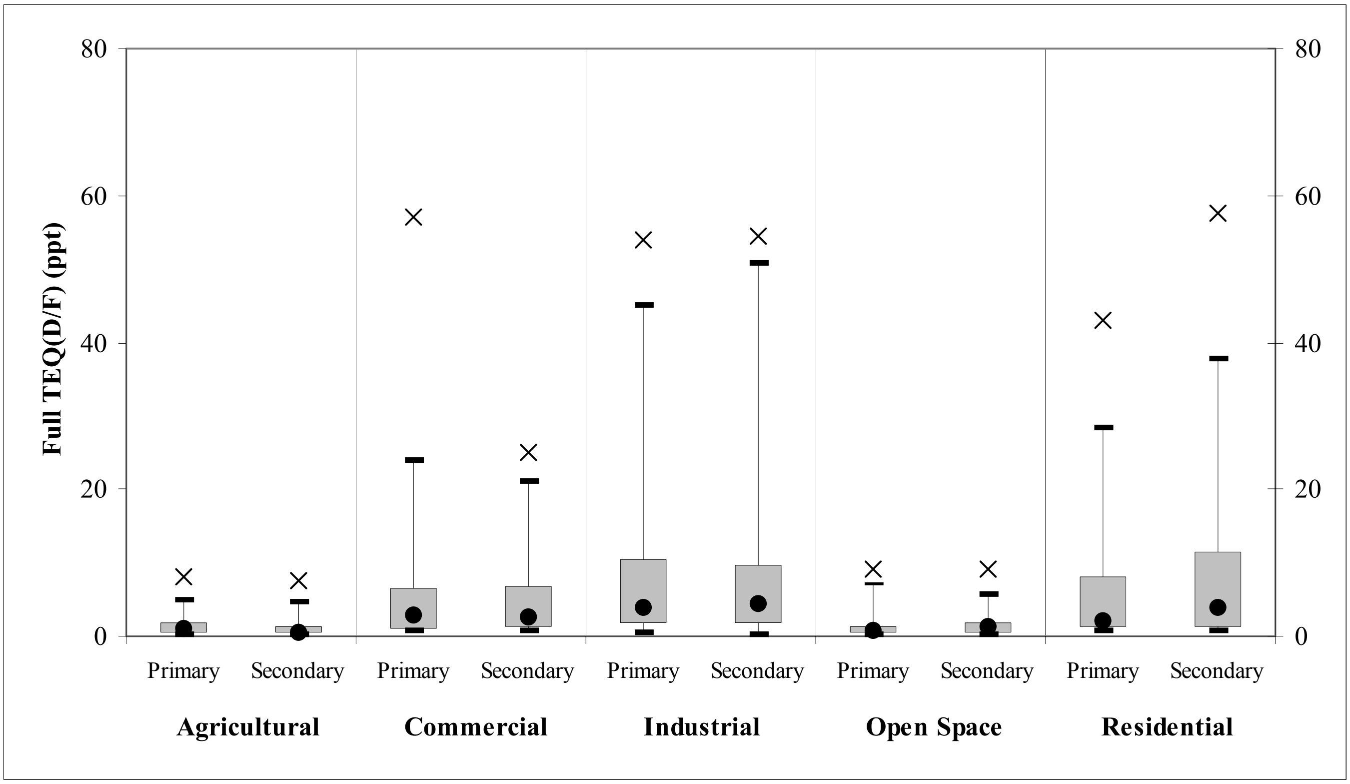
Binding of dioxins to soil particles is a physical process that might be expected to depend on the total organic carbon (TOC) content of the soil, as well as the surface-area-to-mass ratio (i.e., the particle size distribution). Such a dependence of TEQ levels on soil characteristics has been noted by Rogowski et al. (1999), although these data are somewhat limited by use of TEQ values calculated from congener concentrations that were largely below the MDL.

Figure 7 (Panel A) summarizes the relationship between Full TEQ(D/F) and soil TOC. As seen, TOC levels ranged from about 0.2% to 10% in the soil samples, while Full TEQ(D/F) levels ranged from about 1 to 60 ppt. The slope of the best-fit linear regression line through the data is statistically different from zero ($p < 0.01$), but the coefficient of determination is low ($R^2 = 0.109$). This suggests that the TEQ value in a soil sample may depend in part on the TOC of the soil, but that this is not the main determinant of the TEQ value.

Figure 7 (Panel B) shows the relation between Full TEQ(D/F) and the mass fraction of the raw field sample that passes a fine screen. As above, even though the slope of the best-fit linear regression line is statistically different from zero ($p < 0.02$), the coefficient of determination is very low ($R^2 < 0.001$), suggesting that soil particle size distribution is only a minor determinant of TEQ.

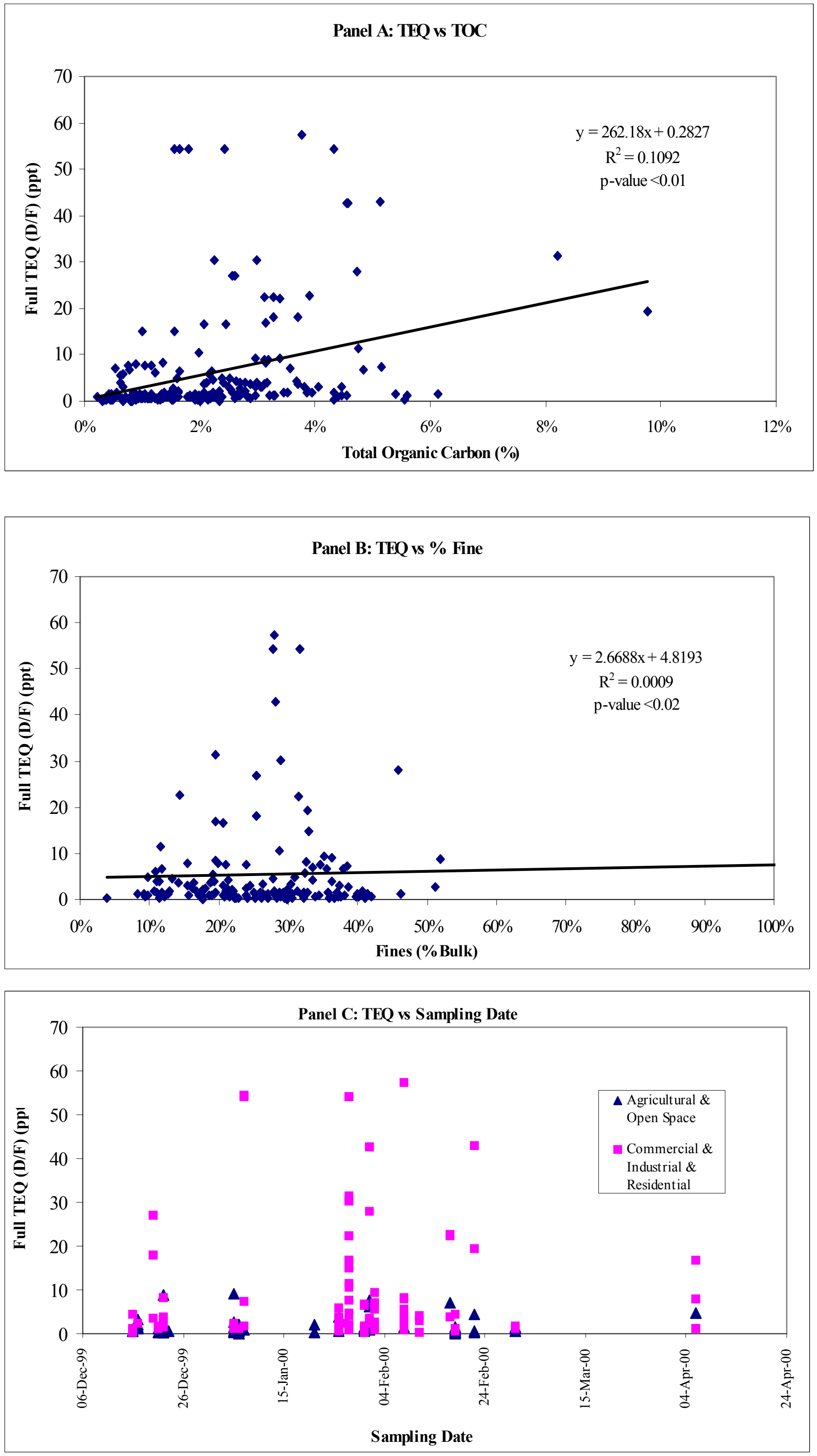
Even though dioxins tend to be relatively stable in the environment, it is possible that levels in soil vary as a function of time due to seasonal differences in emission rates and/or environmental transport rates. Figure 7 (Panel C) shows the Full TEQ(D/F) for the soil samples collected during this study plotted as a function of the sample collection date. As seen, there is no clear pattern, although there is an apparent tendency for the highest values to occur in industrial/commercial/residential samples collected in January or February. Further study would be needed to determine if this is a random or authentic variation as a function of collection date.

Figure 6. Effect of Land Use Re-Classification on TEQ Patterns



Primary = Original Land Use Assignment
Secondary = Alternate Land Use Assignment

Figure 7. Dependence of TEQ on Soil Characteristics



4.3 Comparison to Human-Health Based Guidelines

Although the basic purpose of this study was to characterize the distribution of dioxin samples in soils from the Denver Front Range area (and not to perform a health risk evaluation), it may nevertheless be of some use to provide a health-based frame of reference by which the distributions may be placed in context.

The USEPA has currently established a default concentration value of 1,000 parts per trillion (ppt) TEQ in surface soil as a concentration that is not of cancer or non-cancer concern for lifetime exposure of residents (USEPA 1998a), even when no other site-specific data are known. For commercial and industrial land uses, USEPA guidelines identify 5,000 to 20,000 ppt TEQ as the concentration of concern in soil. These soil screening concentrations are based only upon the 17 TCDD-like PCDDs and PCDFs, calculated using the TEFs for mammals recently recommended by the WHO (Van den Berg et al. 1998).

The Agency for Toxic Substances and Disease Registry (ATSDR) has also established an interim policy guideline for human (residential) exposure to dioxin and dioxin-like compounds in soil (De Rosa et al. 1997). ATSDR identifies a concentration of 50 ppt TEQ in soil as a "screening level," below which no further investigation or characterization will usually be required. ATSDR identifies a concentration of 1,000 ppt TEQ as an "action level," indicating that public health actions such as surveillance, research, health studies, community education, or exposure investigations should be considered. Concentrations between 50 ppt and 1000 ppt TEQ are identified as "evaluation levels," indicating that further investigation of site-specific factors regarding the extent and possible public health implications of the exposure may be warranted.

The USEPA is in the process of completing a comprehensive reassessment of dioxin toxicity, and has tentatively concluded that the carcinogenic and non-carcinogenic potency of dioxins may be somewhat greater than previously believed (USEPA 2000). However, until a complete peer review and cross-program policy assessment of the impacts of this report can be performed, USEPA recommends that the 1,000 ppt TEQ concentration in surface soil continue to be used as a soil screening level for residential land uses (USEPA 1998a), and that 5,000 ppt TEQ be used as a frame of reference for assessing exposure of commercial workers.

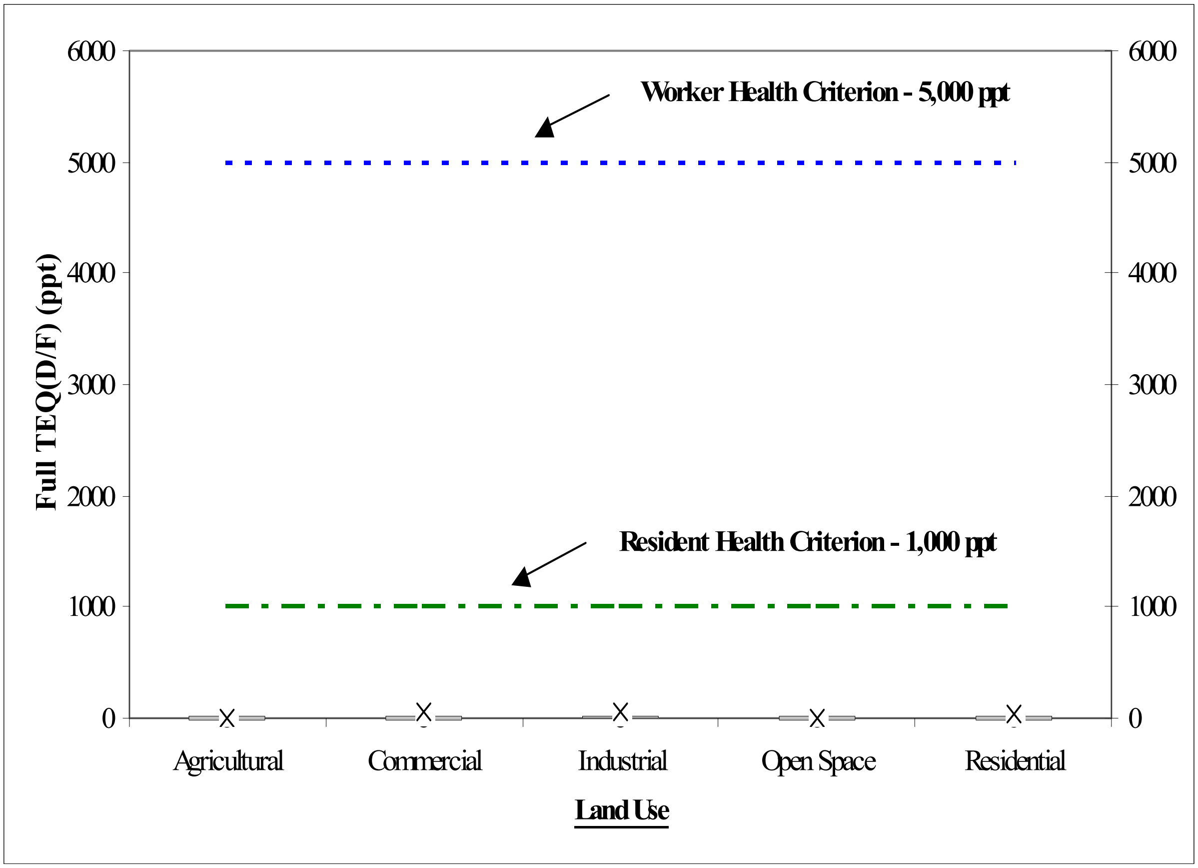
As seen in Table 6 and illustrated graphically in Figure 8, none of the samples collected from the greater Denver Front Range study area approach or exceed the USEPA level of concern for either residents (1,000 ppt TEQ) or workers (5,000 ppt TEQ). Of the 38 samples where land use was classified as residential, only one exceeds the ATSDR "screening level" of 50 ppt TEQ, and none approach the ATSDR "action level" of 1,000 ppt TEQ. As discussed above, this one residential value that exceeds the ATSDR "screening level" appears to be an outlier, even though no apparent local point source was identified for this sample. In addition, like all the samples in this category, it is not from an actual private residence where exposure is estimated to occur for 24 hours per day, 7 days per week. In consideration of these factors, USEPA has determined that dioxin levels in Denver Front Range "background" samples are not of significant human health concern for any land use category.

5.0 SUMMARY AND CONCLUSIONS

The results of this study provide a reliable set of dioxin measurements in a variety of soil sampling locations in the Denver Front Range area. The mean value for Full TEQ for dioxins and furans across all samples was about 5-6 ppt, with individual values ranging from less than 1 ppt TEQ up to a maximum of 57 ppt TEQ[1]. Values from open space and agricultural areas tended to be the lowest, while values from industrial, commercial, and residential areas included some higher values. None of the samples collected approached or exceeded the level of health concern for either residents or workers.

[1] Two samples were collected which had TEQ values of 140 and 155 ppt, but these were judged to be outliers that were not representative of typical ambient levels due to non-point sources.

Figure 8. Full TEQ(D/F) Levels in Front Range Soils Compared to Health Criteria



6.0 REFERENCES

BC Environment. 1995. Dioxins and furans in the British Columbia environment. Report prepared for the Environmental Protection Department, British Columbia Environment, Victoria, British Columbia.

De Rosa CT, Brown D, Dhara R, Garrett W, Hansen H, Holler J, Jones D, Jordan-Izaguirre D, O'Conner R, Pohl H, Xintaras C. 1997. Dioxin and Dioxin-Like Compounds in Soil, Part 1: ATSDR Interim Policy Guideline. Toxicol. Ind. Health 13:759-768.

EBASCO. 1994. Final Integrated Endangerment Assessment/ Risk Characterization (IEA/RC). Version 4.2. July 1994.

Kjeller LO, Jones KC, Johnston AE, and Rappe C. 1991. Increases in the polychlorinated dibenzo-p-dioxin and -furan content of soils and vegetation since the 1840s. Environmental Science and Technology 25:1619-1627.

MRI. 1992. Multivariate statistical analyses of dioxin and furan levels in fish, sediment and soil samples collected near resource recovery facilities, final report. Report produced by Midwest Research Institute (MRI) for Connecticut Department of Environmental Protection, Water Compliance Unit.

NIH. 1995. Expert panel: Report on the impact and assessment of medical and pathological waste incineration on the Bethesda, Maryland, campus of the National Institutes of Health. Report prepared for the National Institutes of Health (NIH) by EEI, Alexandria, Virginia.

Rappe C and Kjeller L. 1987. PCDDs and PCDFs in environmental samples, air particulates, sediments and soil Chemosphere 16:1775.

Reed, LW, Hunt, GT, Maisel, BE, Hoyt, M, Keefe, D, and Hackney, P. 1990. Baseline assessment of PCDDs/PCDFs in the vicinity of Elk River, Minnesota generating station. Chemosphere 21:159-171.

Rogowski, D, Golding, S, Bowhay, D, and Singleton, S. 1999. Screening survey for metals and dioxins in fertilizer products and soils in Washington State. Report prepared for the Washington State Department of Ecology. Ecology Publication No. 99-309. April 1999.

Rogowski, D and Yake, B. 1999. Addendum to the Final Report: Screening survey for metals and dioxins in fertilizer products and soils in Washington State. Report prepared for the

Washington State Department of Ecology. Ecology Publication No. 99-333. November, 1999.

Rotard, W, Christmann, W, and Knoth, W. 1994. Background levels of PCDD/F in soils of Germany. Chemosphere 29:2193-2200.

Schuhmacher, M., Granero, S., Llobet, J. M., de Kok, H. A., and Domingo, J. L. 1997. Assessment of baseline levels of PCDD/F in soils in the neighborhood of a new hazardous waste incinerator in Catalonia, Spain. Chemosphere 35:1947-58.

Tewhey Associates. 1997. Letter to Maine Department of Environmental Protection concerning soil sampling data collected from the Yarmouth Pole Yard Site in November, 1996

USEPA. 1989. Risk Assessment Guidance for Superfund. Volume I. Human Health Evaluation Manual (Part A). United States Environmental Protection Agency, Office of Emergency and Remedial Response. EPA/540/1-89/002. December 1989.

USEPA. 1992. Guidance for Data Useability for Risk Assessment (Part A). U. S. Environmental Protection Agency, Office of Emergency and Remedial Response. Publication 9285.7-09A. April, 1992.

USEPA. 1994. Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and Related Compounds. Volume III of III. Office of Health and Environmental Assessment Office of Research and Development. External Review Draft. August 1994. EPA/600/BP-92/001c.

USEPA. 1996. Columbus waste-to-energy municipal incinerator dioxin soil sampling project. Chicago, Illinois: United States Environmental Protection Agency, Region 5.

USEPA. 1998a. Approach for Addressing Dioxins in Soil at CERCLA and RCRA Sites. OSWER Directive 9200.4-26. Memo from Timothy Fields Jr. April 13, 1998.

USEPA. 1998b. The Inventory of Sources of Dioxin in the United States. Review Draft. USEPA Office of Research and Development. EPA/600/P-98/002Aa. April 1998.

USEPA. 1999. Quality Assurance Project Plan for the Denver Front Range Dioxin Study. Prepared by USEPA Region 8 with technical input form ISSI Consulting Group, Inc., and Gannett Fleming, Inc. December, 1999.

USEPA. 2000. Interim Final Draft: Exposure and Health Assessment for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds. United States Environmental Protection Agency, National Center for Environmental Assessment (NCEA). May 1, 2000.

Van den Berg M, Birnbaum L, Bosveld ATC, Brunström B, Cook P, Feeley M, Giesy JP, Hanberg A, Hasegawa R, Kennedy SW, Kubiak T, Larsen JC, van Leeuwen FXR, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenk D, Tillitt D, Tysklind M, Younes M, Wærn F, Zacharewski T. 1998. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. Environmental Health Perspectives 106:775-792.